Isomerization of Hexene-1 Catalyzed by Ruthenium(III), Rhodium(III), and Palladium(II) Chlorides

Double bond migration of olefins is catalyzed by group VIII metal complexes in solution (*1*). Among group VIII metal chlorides of the second series, rhodium(III) chloride and palladium(II) chloride complex have been reported to be effective for isomerization of olefins (*2*). However, contradictory results have been obtained on the catalytic activity of ruthenium(III) chloride (*2, 3*). The present paper reports the results of a kinetic study of the isomerization of hexene-1 catalyzed by rhodium(III), ruthenium(III), and palladium(II).

The solvents used for the homogeneous reaction systems were benzene for bis(benzonitrile)palladium chloride complex, and ethanol for both ruthenium trichloride trihydrate and rhodium trichloride trihydrate. The reaction was carried out in ampoules at a catalyst concentration of 0.5 mole % to the substrate at 65°C.

The catalytic activity varied widely among these three metal chlorides. The times of reaching equilibrium among the hexene isomers were approximately 15 min for rhodium, 150 min for palladium, and 1000 min for ruthenium as shown in Figs. 1, 2, and 3.

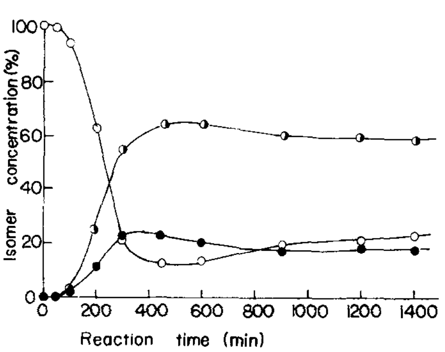

FIG. 1. Isomerization of hexene-1 catalyzed by ruthenium trichloride trihydrate in ethanol solution at 65°C: catalyst concentration, 0.5 mole % of hexene. ○, hexene-1 + *trans*-hexene-3; ◑, *trans*-hexene-2 + *cis*-hexene-3; ●, *cis*-hexene-2.

In the case of ruthenium catalyst an induction period was observed distinctly (about 1 hr). The color of the reaction solution catalyzed by ruthenium(III) chloride changed from a dark brown to a deep greenish blue in a reaction time of about 1 hr. The deep greenish blue is due to ruthenium(II) species. Corresponding to this change, the formation of *n*-hexanal and *n*-hexanone were confirmed in the reaction mixture by glpc. These facts suggest that

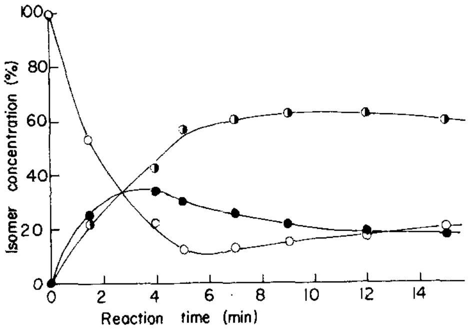

FIG. 2. Isomerization of hexene-1 catalyzed by rhodium trichloride trihydrate in ethanol solution at 65°C: catalyst concentration, 0.5 mole % of hexene.

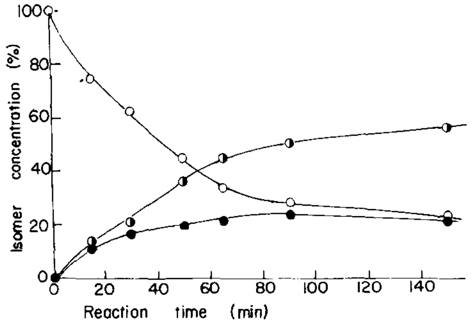

FIG. 3. Isomerization of hexene-1 catalyzed by bis(benzonitrile) palladium chloride in benzene solution at 65°C: catalyst concentration, 0.5 mole % of hexene.

ruthenium(III) was reduced to ruthenium(II) by hexene in the induction period and that the active species for the isomerization is a ruthenium(II) complex. The similar direct reduction of ruthenium(III) by olefin to ruthenium(II)–olefin complexes in ethanol solution has been reported for dienes such as norbornadiene or cyclooctadiene (*4, 5*).

Rhodium(III) chloride is a much more effective catalyst than ruthenium(III) chloride. The induction period was not observed. Cramer and Lindsey (*6*) claimed that rhodium(III) could be reduced to rhodium(I) by olefin or by ethanol, and that this was essential to the catalyst activity for isomerization. We observed the formation of *n*-hexanal and *n*-hexanone in the initial stage of reaction (in 15 sec at 65°C), which were detected by glpc. Consequently, the following reaction can be proposed.

$$2RhCl_3 3H_2O + 6C_6H_{12} \rightarrow (C_6H_{12})_4Rh_2Cl_2 + 2C_6H_{12}O + 4HCl + 4H_2O$$

The brown precipitate which was assumed to be $(C_6H_{12})_4Rh_2Cl_2$ was isolated in the initial stage, but it was too unstable to be characterized. The induction period for isomerization, i.e., the time necessary to produce a sufficient concentration of $(C_6H_{12})_4Rh_2Cl_2$ by the reaction where rhodium(III) was reduced to rhodium(I), was too short at 65° to be observed. The active species of the isomerization catalyst is reasonably associated with the hexene–rhodium(I) complex.

The effect of other ligands was studied on palladium chloride catalyst. The retarding effect of the reagents were in the order triphenylphosphine > triethylamine > pyridine > quinoline > 1,3-cyclooctadiene. Addition of an equimolar amount of 1,3-cyclooctadiene to palladium chloride complex retarded the rate about one third of the uninhibited rate. Equimoles of triphenylphosphine added to palladium(II) inhibited the reaction almost completely. These reagents occupy the coordination site for hexene. The sequence of retarding effects seem to follow reasonably the coordinating strength of the reagents, as indicated by the stabilities of silver(I) complex (*7, 8*).

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HIDEFUMI HIRAI
HIROAKI SAWAI
EI-ICHIRO OCHIAI
SHOJI MAKISHIMA

Department of Industrial Chemistry, Faculty of Engineering,
University of Tokyo
Bunkyo-ku, Tokyo, Japan

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